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Facilities for Development of Modified Nitride-Based Fuel Pellets

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Abstract - *Facilities to support development of modified nitride-based reactor fuel pellets have been activated and are now in operation at Lawrence Livermore National Laboratory. These facilities provide the controls and monitored laboratory conditions required to produce, evaluate, and verify quality of the nitride-based product required for this fuel application. By preserving the high melting point, high thermal conductivity, and high actinide density properties of nitride fuel while enhancing stoichiometry, density, and grain structure, and by applying inert matrix (ZrN) and neutron absorbing (HfN) additives for improved stability and burn-up characteristics, the requirements for a long-life fuel to support sealed core reactor applications may be met.*

This paper discusses requirements for producing the modified nitride powders for sintering of fuel pellets, translation of these requirements into facility specifications, and implementation of these specifications as facility capabilities.

I. INTRODUCTION

In support of the US National Energy Policy of 2001[1], advanced fuel and fuel cycle technologies that are cleaner, more efficient, less waste-intensive, and more proliferation resistant should be developed.

The need for advanced fuel development is emphasized in DOE-supported programs, e.g., Advanced Fuel cycle Initiative (AFCI)[2], GEN-IV Initiative[3], and Nuclear Energy Research Initiative (NERI)[4]. Lawrence Livermore National Laboratory (LLNL) is interested in advanced fuel research and manufacturing using its multi-disciplinary capability and facilities to support a design concept for a small, secure, transportable, and autonomous reactor (SSTAR)[5].

SSTAR is a compact, liquid-metal cooled, fast reactor. The reactor has a sealed core vessel that could be shipped to the user and returned to the supplier having never been opened in its long operating lifetime. This sealed reactor concept envisions no fuel refueling nor on-site storage of spent fuel, and as a result, can greatly enhance proliferation resistance. To support a sealed and long-life core, selection of suitable fuel, cladding and core internal materials is essential. A nitride-based fuel is selected for SSTAR because nitride has properties suitable for fast reactor. Its thermal conductivity is 10 times higher than oxide (23 W/m^{o}K for UN vs. 2.3 W/m^{o}K for UO2 at 1000 ^{o}K)[6] and its melting temperature is much higher than that of metal fuel (2800 ^{o}C for PuN vs. 650 ^{o}C for Pu metal). The perceived concern for a potential positive reactivity void coefficient due to the decomposition of nitride fuel can be mitigated by the use of ^{15}N-enriched nitrogen.

Cladding for the nitride fuel, though not considered in the current research, is important as it provides an interface between the fuel and coolant and a barrier to prevent fission gas release during normal and accidental conditions. In fabricating the nitride fuel rods and assemblies, the cladding material should be selected based on its corrosion-resistant properties, the chemical/physical interaction with the nitride fuel, and its thermal and neutronic properties.

The US NASA space reactor, the SP-100[7] was designed to use mono-uranium nitride (UN) fuel. UN fuel pellets were manufactured for SP-100 with Nb-1-Zr cladding and Re liner. Many UN fuel assemblies were irradiated in fast-spectrum test reactors (FFTF and EBR-II) with good irradiation results. The Russian Naval submarines also use nitride fuel with HT-9 cladding in Pb-Bi coolant. The operating experience of the Russian submarine is not readily available, however, such combination of fuel, cladding and coolant was proposed by Russia for a commercial-size liquid-metal cooled fast reactor (BREST)[8].

II. OBJECTIVE

Facilities to support the manufacturing of nitride-based fuel pellets have been activated and are now in operation at LLNL. The objective of the research is to manufacture nitride fuel with desired properties in stoichiometry, density, and grain structure and with additives (ZrN and HfN, etc.) for improved stability and high burn-up characteristics. These properties and characteristics are required to support the long-life nitride fuel for a sealed reactor core. The research on

uranium nitride fuel is carried out in the following phases:

- Facility Development:
  Essential facility (glove box, furnace and hood, and analysis capabilities) and equipment (grinder, binder, press, etc.) are assembled and tested. Process requirements and specifications for implementation are developed.

- Nitride Fuel Manufacturing:
  Mono-uranium nitride (UN) and modified UN (with additives ZrN and HfN) are manufactured, with compositions and fuel specifications predicted by analytical results.

- Fuel Irradiation and Testing:
  Samples of the manufactured fuel pellets are intended for irradiation in UC Davis's research reactor housed in McClellan Nuclear Radiation Center, followed by post irradiation examination (PIE).

This paper describes the first phase activities with focus on development of process requirements and implementation specifications.

1.0 Process requirements

Uranium nitride powder for the manufacture of fuel pellets, can be synthesized by a number of processes: metal/nitration, metal hydride/ nitration, metal oxide/ carbothermic reduction/nitration, as well as processes starting with metal fluorides or chlorides.[9] High burnup uranium nitride fuel pellets, regardless of the process used in producing the UN powder, should exhibit the following property related characteristics. The UN powder should sinter to greater than 90% full theoretical density. It should produce a predominantly closed pore structure and a relatively large (greater than 40 micron) grain size. The UN should maintain near stoichiometric composition to avoid formation of sesquinitride at one extreme or metallic uranium at the other. Maintained UN stoichiometry and low levels of excess oxygen and carbon impurity, in both powder and final sintered fuel pellet form, are viewed as conducive to achieving sinterability, improved pellet thermal stability and reduced pellet/cladding interaction. [10, 11, 12]

Metal and metal hydride nitration processes typically produce UN having oxygen at levels of 100-700 ppm (parts per million) and carbon at 70-500 ppm. This is considered an acceptable residual oxygen and carbon impurity level for UN. [10, 11, 12] The UN produced by carbothermic reduction, using the process proposed by Greenhalgh, et.at.[13,14], typically contains 1000 ppm oxygen and 2000 ppm carbon. Muromura and Tagawa modified the carbothermic reduction process by adding a reducing gas component (H_2 or NH_3) that results in impurity levels in the UN (oxygen plus carbon) in the range of 500-1000 ppm combined. [15, 16], achieving UN processing capabilities for oxygen and carbon management equivalent to metal and metal hydride nitration. This process, scaled to laboratory-sized operations, can be implemented in a cost effective way. By this criteria, the carbothermic synthesis process was selected as the basis for facility design.

In order to maintain these levels of purity, the handling of powders and pellets during UN synthesis, grinding, pressing, and sintering must be accomplished within a dry N_2 atmosphere having less than 10 ppm O_2.

Process requirements for grinding, blending, and granulation are defined by the process bounds investigated by Matthews, et.al. [12] A conventional vibratory ball mill fulfills this requirement. The reactive nature of UN in air requires that these operations be performed in a dry N_2 atmosphere. Placing the ball mill in the N_2 atmosphere requires that the mill motor and switches be designed to operate under those conditions. Powder grinding and blending capability is enhanced with the ability to pass a reactive process gas (N_2, H_2/N_2 mixture) or inert flush gas (Ar, He) through the milling jar during the milling process.[17, 18] This capability is included as a process requirement.

The pressing of green uranium nitride pellets that sinter to target densities has been demonstrated at pressures of 50 ksi.[11] Again, due to the reactivity of UN with air, pressing must take place in a dry N_2 atmosphere.

The published literature[11, 12, 19, 20] demonstrates that UN can be sintered to greater than 90% full theoretical density at process temperatures of 1650 C within 12 hours sintering time. UN can optionally be sintered in N_2 atmosphere to correct for hypo-stoichiometry or Ar atmosphere to eliminate excess N_2 and avoid formation of sesquinitride and resultant cracking.

However, the sintering requirements that dictate that the sintering furnace be operated at 1650 C. also sets performance requirements on the $MoSi_2$ heater elements. The furnace heater elements must operate in air to maintain required maximum performance.

The process diagram shown in Figure 1 integrates these requirements for synthesis, grinding, pressing, and sintering. The diagram was developed to provide a primary tool for assessing the requirements and defining specifications for laboratory scale production and to define analytical capabilities needed to support the nitride based fuel development. The diagram in general identifies process mixtures and conditions within each process operation. The furnace process operations (blue boxes) do not define a time-based sequence of process

steps. The furnace operations do define process changes and process effluents resulting from these changes.

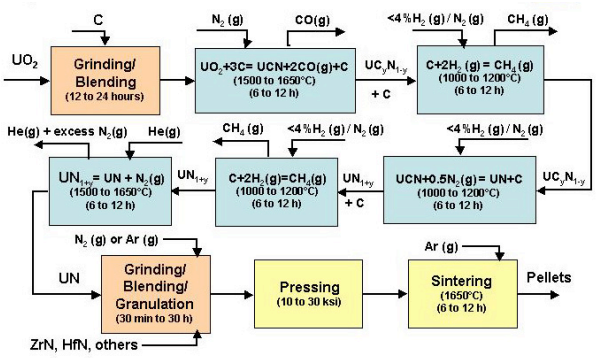

Figure 1. UN pellet fabrication process diagram.

The process diagram also indicates the need to control quality and purity of materials (process inputs). As an example, UO_2 oxidizes when stored in air. The lattice parameter for uranium oxide (fluorite lattice structure) decreases with increased oxygen content.[21] X-ray diffraction (XRD) of as-received UO_2 can indicate hyper-stoichiometry as high as $UO_{2.18}$. Therefore, the as-received uranium oxide should be furnace reduced back to near-stoichiometry and verified by XRD, to minimize this source of excess oxygen. Likewise, the carbon is certified to 99.999% purity to minimize other process contamination, and all process gases are certified for purity.

2.0 Facility specifications

The preceding process requirements translate into specifications for hardware performance requirements and analytical capabilities to support nitride based fuel development. These are as follows:

Grinding/Blending (in glove box):
- Dry clean N_2 atmosphere
- Reactive gas ball milling (N_2, H_2/N_2, He)
- Process gas analysis capability

Furnace processes/Sintering (not in glove box):
- Sealed furnace tube (N_2, H_2/N_2, He, Ar)
- Air atmosphere for heater elements ($MoSi_2$)
- Controlled process flow rate (N_2, H_2/N_2, He, Ar)
- Programmed operation to 1650C for 30+ hrs
- Logged furnace temperature data
- Process gas analysis capability

Glove box:
- Dry, clean N_2 atmosphere (less than 10 ppm O_2)
- Oxygen monitor to verify box atmosphere
- Purged (dry N_2) large volume load chamber
- Low heat load (furnace outside of glove box)
- Precision balance, press, disassembly area

Press (in glove box):
- 50 ksi green compacting die pressure
- Dry, clean N_2 atmosphere (less than 10 ppm O_2)

Material certification:
- Verification of process material quality
- Certification of process gas sources

Gas analysis:
- Gas mass spectrometry
- Logged process monitoring

Sample analysis:
- X-ray diffraction to identify phases
- Photo-spectrometry for N_2, O_2, C content
- Pycnometry
- Ceramography
- Scanning electron microscopy
- Support laboratories

3.0 Facility implementation

The facilities to support nitride fuel development have been implemented within three primary facility components: glove box, furnace hood, and analysis capabilities (gas analysis cart, distributed data collection, analytical support labs) shown in Figure 2.

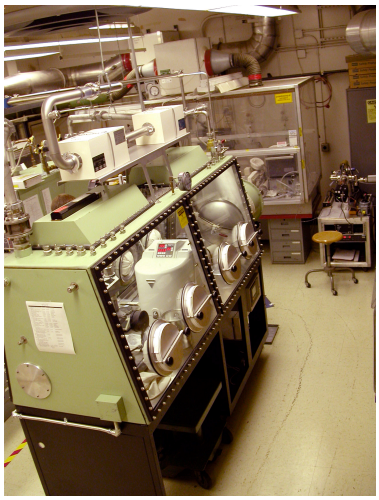

Figure 2. Nitride facilities: glove box (foreground), furnace hood (background), and gas analysis cart (right). Note: HEPA filtered exhaust.

The glove box provides the capacity for locating all of the non-furnace operations within one dry, clean N_2 atmosphere. It consists of the glove box enclosure, a Dri-train catalytic bed and molecular sieve, and a clean N_2 source. The glove box N_2 atmosphere circulates through the VAC dual bed Dri-train shown in Figure 3, which removes both oxygen and water contaminants.

Figure 3. Dri-train catalytic bed and molecular sieve.

A DeltaF process oxygen analyzer installed on the glove box provides continuous glove box oxygen level monitoring. The glove box and Dri-train typically indicate oxygen levels less than 5 ppm and can operate for two weeks between Dri-train bed regenerations. The dual bed configuration allows one bed to be regenerated while the other remains in service.

The glove box contains: a 24,000 lb. Carver hydraulic laboratory press, a Fritch "pulverisette 6" planetary ball mill with purge gas capability, a certified balance, and workspace to perform furnace tube handling operations.

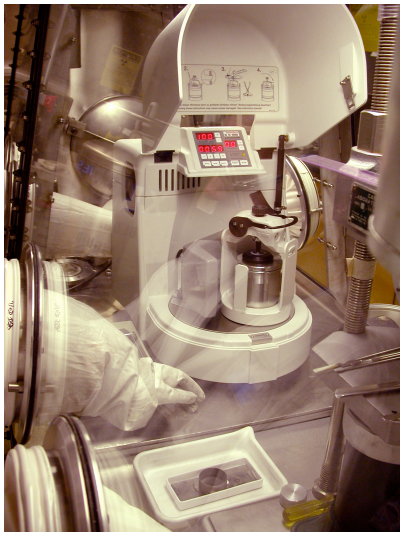

Figure 4. Fritch mill with Carver press in foreground.

The glove box is equipped with the air-lock shown in Figure 5. The port can be evacuated to the millitorr pressure range and backfilled with N_2, or purged with N_2 until the air in the lock is diluted to ppm O_2 levels. The air-lock provides capability to move the sealed furnace tube from glove box to furnace.

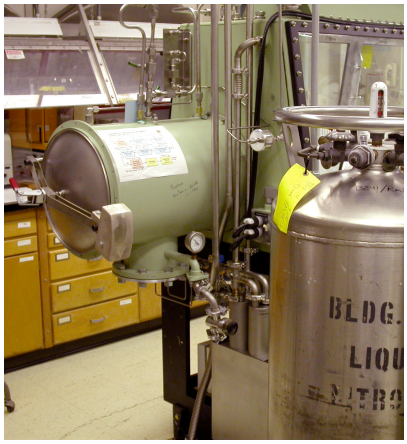

Figure 5. Glove box air-lock port with N_2 dewar in foreground.

The furnace is located within the furnace hood positioned across from the air-lock port entry to the glove box. The sealed furnace tube moves between glove box and furnace hood during normal operations. The tube is handled only when at room temperature.

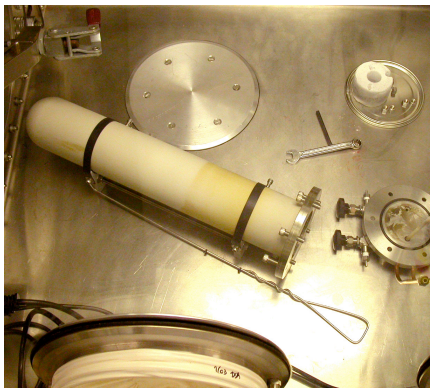

Figure 6. Unsealed furnace tube in glove box.

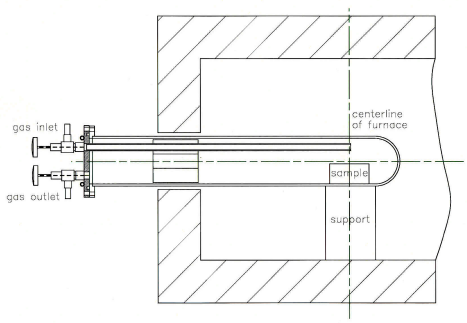

Figure 7. Schematic of sealed tube placed in furnace.

During furnace operation, purge gas from the gas outlet is configured to prevent backflow infiltration. This gas flow is continuously sampled and analyzed using an Inficon Transpector Residual Gas Analyzer (RGA) during furnace operation. Mass distribution of gas species and furnace temperature are continuously logged using Labview and vendor software. The RGA cart can also monitor purge gas from the outlet of the Fritsch ball mill during reactive milling. This system has been tested using blend gases and has been demonstrated to provide adequate mass resolution for these real-time process measurements.

Following post-run disassembly of the sealed tube in the glove box, material samples are set aside for analysis and verification of results. Initial powder samples are routinely taken to support laboratory facilities for verification of phases by x-ray diffraction (XRD) and evaluation of composition by x-ray photoemission spectrometry (XPS). High density sintered parts are checked for density by pycnometry. Microstructures are documented on ceramographs. Scanning electron microscopy (SEM) is used to characterize appropriate features. This suite of analytical tools is routinely called on as data analysis requires.

III. CONCLUSION

Facilities supporting development on UN based fuel materials at LLNL have been installed, tested, qualified for operation, and are currently in use, having met all safety and performance requirements for their activation. Qualification tests on essential facilities and equipment (glove box, furnace, and analytical capability) show that these systems meet all performance and operational requirements for this material development effort.

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